

AD-A203 474

DTIC FILE COPY

4

OFFICE OF NAVAL RESEARCH

Contract N00014-87-K-0288

Task No. NR 634-840

R&T Code 413j007

TECHNICAL REPORT NO. 3

The First Transition Metal Isonitrilate:
Synthesis and Characterization of $K[Co(2,6-Me_2C_6H_3NC)_4]$

Garry F. Warnock and N. John Cooper

Prepared for Publication
in the
Journal of the American Chemical Society

Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

January 5, 1989

DTIC
ELECTRONIC
JAN 12 1989
S H

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

89

1 12 017

REPORT DOCUMENTATION PAGE

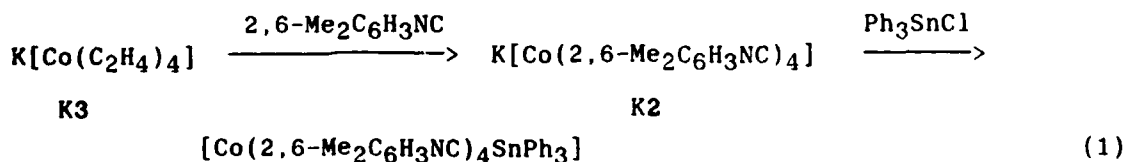
1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6a NAME OF PERFORMING ORGANIZATION Chemistry Department University of Pittsburgh		6b OFFICE SYMBOL (If applicable)	7b ADDRESS (City, State, and ZIP Code) (Code 1113) 800 North Quincy Street Arlington, VA 22217-5000		
6c ADDRESS (City, State, and ZIP Code) Pittsburgh, PA 15260		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-K-0288			
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS		
8c ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO	PROJECT NO	TASK NO NR634-840	WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) The First Transition Metal Isonitrilate: Synthesis and Characterization of $K[Co(2,6-Me_2C_6H_3NC)_4]$					
12 PERSONAL AUTHOR(S) Warnock, Garry F.; Cooper, N. John					
13a TYPE OF REPORT Technical Report		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Year, Month, Day) 1989 January 5	
15. PAGE COUNT 10					
16 SUPPLEMENTARY NOTATION Prepared for Publication in J. Am. Chem. Soc.					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	homoleptic isonitrile complex, cobalt (1) complex compounds, isonitrilate. (A191) ←		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Addition of 4 equiv of 2,6-Me ₂ C ₆ H ₃ NC to K[Co(C ₂ H ₄) ₄] in THF results in displacement of the ethylene and formation of the homoleptic isonitrilate [Co(2,6-Me ₂ C ₆ H ₃ NC) ₄] ²⁻ (2 ⁻), isolated as K ₂ , [K(DME)] ₂ , and [K(18-crown-6)] ₂ . IR and ¹ H NMR spectra are consistent with formulation of 2 ⁻ as a complex of terminal isonitrile ligands, and chemical characterization of 2 ⁻ was provided by addition of Ph ₃ SnCl in THF to give [Co(2,6-Me ₂ C ₆ H ₃ NC) ₄ SnPh ₃] (4).					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL			22b TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

Isonitriles, like carbon monoxide, interact synergistically with transition metal centers and can balance σ donation to the metal from a carbon based orbital with π back donation into an antibonding orbital of the isonitrile ligand,¹ and there is an extensive chemistry of transition metal isonitrile complexes². It is, however, generally believed, largely on the basis of spectroscopic³ and electrochemical⁴ studies, that isonitriles are better σ donors and poorer π acceptors than CO, consistent with the observation that typical homoleptic isonitrile complexes of many metals are in higher oxidation states than the typical carbonyl complexes of the same metals. In the case of cobalt, for example, a range of stable homoleptic isonitrile complexes of Co(I) have been known for years,⁵ and there is at least one reliable early report of a homoleptic complex of Co(II),⁶ but the first homoleptic Co(0) isonitrile complexes, isoelectronic with $[\text{Co}_2(\text{CO})_8]$, were not reported until 1977,⁷ and there are no reports of isonitrile analogues of $[\text{Co}(\text{CO})_4]^-$ nor indeed of any other transition metal isonitrilates.⁸

The mild description of Co(0) isonitrile complexes as "air-sensitive even in the solid state"^{7c} and the accessibility of Co carbonyls in oxidation states as low as -3,⁹ suggested that cobalt isonitrilates should be synthetically accessible. The lack of reactivity of $[\text{Co}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_8]$ (1) towards sodium amalgam^{7b,c} and of $[\text{Co}_2(\text{t-BuNC})_8]$ towards potassium amalgam^{7a,d} indicated, however, that reduction of a zerovalent isonitrile complex was unlikely to provide a successful approach to Co isonitrilates, and ligand substitution within a preformed complex of Co in a negative oxidation state provides the most obvious alternative strategy. The remarkable ethylene complex of Co(-1) reported by Jonas¹⁰ seemed to be an ideal substrate for such an experiment, and we now wish to report the synthesis and characterization of $\text{K}[\text{Co}(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})_4]$, (K2), an unprecedented transition metal isonitrilate, by ethylene displacement from $\text{K}[\text{Co}(\text{C}_2\text{H}_4)_4]$ ¹⁰ (K3):



<input checked="checked" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>		Codes	
		Dist	Avail and/or Special
A-1			



4

In a typical preparation 4 molar equiv. of 2,6-Me₂C₆H₃NC¹¹ (1.35 g, 10.27 mmol) in THF (30 mL) were added to a grey sample of solid K[Co(C₂H₄)₄] (0.54 g, 2.57 mmol) at room temperature. Effervescence indicated immediate reaction and within 5 minutes a deep orange-red solution had formed. IR spectra indicated complete consumption of the free isonitrile ($\nu_{\text{CN}} = 2116 \text{ cm}^{-1}$ in THF), and formation of a complex characterized by an intense, broad absorption centered at 1815 cm⁻¹. This suggested that all of the ethylenes had been displaced to form the potassium salt of the tetra-isonitrilate (Eq. 1), and this was isolated by concentration under reduced pressure to ca. 5 mL and addition of pentane (20 mL) to the stirred solution to precipitate K[Co(2,6-Me₂C₆H₃NC)₄] (K2)¹² (1.17 g, 1.85 mmol = 73%) as an orange powder. In this form the material is extremely air sensitive, and the powder turns black in seconds following exposure to air, but recrystallization from 1,2-dimethoxyethane (DME, 5 mL) by addition of diethyl ether (50 mL) gave a 61% yield (based on K3) of dark crimson parallel-epipeds of a mono-DME solvate [K(DME)][Co(2,6-Me₂C₆H₃NC)₄]¹³ which, although they still decomposed in air in minutes, were significantly easier to handle than the unsolvated powder.

Formulation of K2 as an isonitrilate containing terminal isonitrile ligands, although awaiting structural confirmation, is strongly supported by IR spectra of K2 in THF, which are dominated by broad absorptions centered at 1890 (sh) and 1815 (vs) cm⁻¹. These bands are ca. 200 cm⁻¹ below the frequency of the terminal $\nu_{\text{C}\equiv\text{N}}$ stretch in 1,⁷C but over 150 cm⁻¹ above the bridging $\nu_{\text{C}=\text{N}}$ stretch in 1,⁷C consistent with assignment to a stretching absorption of a

terminal C≡N bond which has been dramatically weakened by back-donation from the electron-rich metal center in 2^- . The broadening probably reflects ion pairing effects analogous to those often observed for carbonylmetalates,¹⁴ and this is supported by the reduction in the width at half height of the absorptions from 180 cm^{-1} to 120 cm^{-1} (without a significant shift in position) when one equiv. of 18-crown-6 (18-C-6) was added to a THF solution of K_2 to form $[K(18-C-6)]_2$.¹⁵ The low frequencies of the $\nu_{C\equiv N}$ absorptions in all these salts are consistent with marked bending of the isonitrile ligands similar to that observed for the radial ligands of $[Fe\{CN(t-Bu)\}_5]^{16}$ - it has been suggested that the radial ligands are responsible for the unusually low 1830 cm^{-1} bands of this complex, and that such bending reflects extensive back bonding from the electron-rich metal.¹⁶ The single chemical environment observed for the isonitrile ligands is consistent with the proposed formulation.

Addition of Ph_3SnCl provided chemical characterization of K_2 ,¹⁷ and established that derivatives of 2^- can be prepared by reaction with electrophiles. When a solution of Ph_3SnCl (0.62 g, 1.61 mmol) in THF (30 mL) was added dropwise to a solution of K_2 (1.0 g, 1.61 mmol) in THF (35 mL) at -78°C a transient green color changed to bright yellow as the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure and the product extracted into diethyl ether (200 mL). After filtration the ether was removed under reduced pressure, and the yellow glass solidified by scraping under pentane. The solvent was again removed under reduced pressure to give 1.20 g, 1.28 mmol ($\approx 80\%$) of crude $[Co(2,6-Me_2C_6H_3NC)_4SnPh_3]$ (**4**). Recrystallization from ether (0.8 g in 8 mL) by addition of pentane (240 mL) and cooling to -30°C gave analytically pure **4**¹⁸ (0.55 g, 0.59 mmol) in 69% yield (2 crops).

We have attempted to circumvent the need to prepare the intermediate ethylene complex K_3 by a direct synthesis of K_2 in which **1** is reduced with K/Hg or potassium naphthalenide, but such experiments have been unsuccessful. By

analogy with the preparation of K3¹⁰ we have also examined the reduction of cobaltocene with potassium in the presence of 2,6-Me₂C₆H₃NC, but have been unable to obtain tractable products from this reaction and see no IR evidence for formation of K2 in THF.

The accessibility of stable, crystalline salts of [Co(2,6-Me₂C₆H₃NC)₄]⁻ indicates that the ability of isonitriles to stabilize metals in negative oxidation states has probably been underestimated, and that isonitrilates may have a chemistry as rich as that of metal carbonylates. Substitution of highly reduced precursors with labile alkene ligands offers a high yield and convenient route (and so far the only route) to such complexes, and we are currently exploring the extension of this approach to the synthesis of other cobalt isonitrilates and to isonitrilates of other transition metals.

Acknowledgement. This work was supported in part by the Office of Naval Research.

References

- (1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, CA, 1987, p. 148.
- (2) This has been systematically reviewed at several stages of development:
 - (a) Malatesta, L. Prog. Inorg. Chem. 1959, 1, 283. (b) Malatesta, L.; Bonati, F. Isocyanide Complexes of Transition Metals; John Wiley, New York, 1969. (c) Treichel, P. M. Adv. Organomet. Chem. 1973, 11, 21. (d) Yamamoto, Y. Coord. Chem. Rev. 1980, 32, 193. (e) Singleton, E.; Oosthuizen, M. E. Adv. Orgmet. Chem. 1983, 22, 209.
- (3) Seminal papers include: Bigorgne, M.; Bouquet, A. J. Organomet. Chem. 1963, 1, 101. (b) Horrocks, W. D.; Taylor, R. C. Inorg. Chem. 1963, 2, 723. (c) Cotton, F. A. Inorg. Chem. 1964, 3, 702. (d) van Ecke, G. R.; Horrocks, W. D. Inorg. Chem. 1966, 5, 1960. (e) Horrocks, W. D.; Taylor, R. C. Inorg. Chem. 1965, 3, 584. (f) Strohmeier, W.; Hellmann, H. Chem. Ber. 1964, 97, 1877. (g) Kruck, Th. Angew. Chem. 1967, 79, 27.
- (4) (a) Treichel, P. M.; Firsich, D. W.; Essenmacher, G. P. Inorg. Chem. 1979, 18, 2405. (b) Treichel, P. M.; Dirren, G. E.; Mueh, H. J. J. Organomet. Chem. 1972, 44, 339.
- (5) (a) Malatesta, L.; Sacco, A. Z. Anorg. Chem. 1953, 273, 247. (b) Malatesta, L.; Sacco, A. Ann. Chim. (Rome) 1954, 43, 617. (c) Sacco, A.; Freni, M. Angew. Chem. 1958, 70, 599.
- (6) Pratt, J. M.; Silverman, P. R. Chem. Comm. 1967, 117.
- (7) (a) Barker, G. K.; Galas, A. M. R.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Turney, T. W.; Welch, A. J.; Woodward, P. J. Chem. Soc. Chem. Comm. 1977, 256. (b) Yamamoto, Y.; Yamazaki, H. J. Organomet. Chem. 1977, 137, C31. (c) Yamamoto, Y.; Yamazaki, H. Inorg. Chem. 1978, 17, 3111. (d) Carroll, W. E.; Green, M.; Galas, A. M. R.; Murray, M.; Turney, T. W.; Welch, A. J.; Woodward, P. J. Chem. Soc. Dalton Trans. 1980, 80.

- (8) We propose that homoleptic isonitrile complexes of metals in negative oxidation states be termed "isonitrilates" by analogy with metal carbonylates.
- (9) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. J. Chem. Soc. Chem. Comm. 1977, 686.
- (10) Jonas, K.; Schieferstein, L.; Kruger, C.; Tsay, H. Y. Angew. Chem. Int. Ed. 1979, 18, 550.
- (11) Weber, W. P.; Gokel, G. W.; Ugi, I. K. Angew. Chem. Int. Ed. Engl. 1972, 11, 530.
- (12) IR (Nujol, ν_{CN}): 2005 (vw) 1890 (sh), 1770 (vs) cm^{-1} ; ^1H NMR (CD_3CN) δ 9.55 (t, $J = 7.4$ Hz, 4H, para-H of C_6H_3), 9.68 (d, $J = 7.4$ Hz, 8H, meta-H of C_6H_3), 2.37 (s, 24H, CH_3). Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{CoKN}_4$: C, 69.43; H, 5.83. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 68.78; H, 5.93.
- (13) IR(Nujol, ν_{CN}): 2005 (vw), 1880 (sh), 1815 (vs) cm^{-1} . ^1H NMR spectra in CD_3CN are identical to those of K2, except for the presence of 1.0 ± 0.1 molecules of DME for every 4 isonitrile ligands. Anal. Calcd for $\text{C}_{40}\text{H}_{46}\text{CoKN}_4\text{O}_2$: C, 67.40; H, 6.50. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 67.28; H, 6.60.
- (14) Darensbourg, M. Y. Prog. Inorg. Chem. 1985, 33, 221.
- (15) Analytically pure dark crimson crystals of $[\text{K}(18\text{-C-}6)]_2$ could be obtained in 80% yield (from K2) by recrystallization from THF by addition of diethyl ether, and ^1H NMR spectra in CD_3CN confirmed the presence of 1.0 ± 0.1 molecules of 18-C-6 for every 4 isonitrile ligands. IR (Nujol, ν_{CN}): 2005 (w), 1890 (sh), 1815 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{48}\text{H}_{60}\text{CoKN}_4\text{O}_6$: C, 64.99; H, 6.82; N, 6.32. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 64.78; H, 6.65; N, 6.18.

- (16) (a) Bassett, J. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A. J. Chem. Soc. Chem. Comm. 1977, 853. (b) Bassett, J. M.; Berry, D. E.; Barker, G. K.; Green, M.; Howard, J. A. K. J. Chem. Soc., Dalton Trans. 1979, 1003.
- (17) For leading references on this procedure, including the pioneering studies by Ellis, see: Leong, V. S.; Cooper, N. J. Organometallics 1987, 6, 2000.
- (18) IR (Nujol mull, ν_{CN}): 2110 (w), 2035 (sh), 1992 (s, br) cm^{-1} . ^1H NMR ($\text{CD}_3\text{OCD}_2\text{CD}_2\text{OCD}_3$) δ 7.9 to 6.7 (m, 27H, $\text{C}_6\text{H}_3+\text{C}_6\text{H}_5$), 2.12 (s, 24H, CH_3).
Anal. Calcd for $\text{C}_{54}\text{H}_{51}\text{CoN}_4\text{Sn}$: C, 69.47; H, 5.51; N, 6.00. Found (Dornis u. Kolbe, Mulheim a.d. Ruhr): C, 69.32; H, 5.46; N, 5.91.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1